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FINAL TECHNICAL REPORT

For the period April 1, 1978 ∿ March 31, 1982

CHEMICAL DURABILITY IMPROVEMENT AND STATIC FATIGUE OF GLASSES

Supported by

Office of Naval Research
No. N00014-78-C-0315

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The ~~following~~ following research results were obtained: (1) The rate of corrosion of silica glass by hot alkaline solution was reduced when a small amount of calcium is added to the solution. This inhibitor effect was caused by the deposition of calcium on the glass surface and a protective film formation. Similar but less drastic effect was observed for other alkaline earth elements. When heavy alkaline earth elements such as strontium, barium are contained in the alkaline solution, severe, mechanically damaging surface flow developed.

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2) Mechanical strength of high silica glass was measured in various solvents. The strength varied while the dynamic fatigue susceptibility did not. The strength value correlated well with the surface energy of the glass estimated from swelling of porous high silica glass immersed in solvents.

3) Surface of silica glass was made hydrophobic by chemical reactions. The resulting glasses showed very little tendency of dynamic fatigue.

4) Dissolution rate of silica glass was found to increase under hydrostatic pressure. This appears to contradict with the stress-corrosion mechanism which assumes that the glass corrosion increases with tensile stress and decreases with compressive stress.

5) The strength increase commonly observed for abraded glass immersed in water (crack blunting) was attributed to dissolution-precipitation mechanism rather than to simple dissolution.

6) Dynamic fatigue susceptibility of sodium silicate glasses was found to increase with increasing water content in glass.

I. SUMMARY

The present research program entitled "Chemical Durability Improvement and Static Fatigue of Glasses" was supported by the Office of Naval Research under the contract No. N00014-78-C-0315, from 1 April 1978 to 31 March 1982. The original objective of the research was to improve chemical durability of glass by coating or other means and reduce or eliminate the static f tigue, which was believed to be caused by stress corrosion. Following research results were obtained.

1. The rate of corrosion of silica glass by hot alkaline solution was reduced when a small amount of calcium is added to the solution. This inhibitor effect was caused by the deposition of calcium on the glass surface and a protective film formation. Similar but less drastic effect was observed for other alkaline earth elements. When heavy alkaline earth elements such as strontium, barium are contained in the alkaline solution, severe, mechanically damaging surface flow developed.
2. Mechanical strength of high silica glass was measured in various solvents. The strength varied while the dynamic fatigue susceptibility did not. The strength value correlated well with the surface energy of the glass estimated from swelling of porous high silica glass immersed in solvents.
3. Surface of silica glass was made hydrophobic by chemical reactions. The resulting glasses showed very little tendency of dynamic fatigue.
4. Dissolution rate of silica glass was found to increase under hydrostatic pressure. This appears to contradict with the stress-corrosion mechanism which assumes that the glass corrosion increases with tensile stress and decreases with compressive stress.

5. The strength increase commonly observed for abraded glass immersed in water (crack blunting) was attributed to dissolution-precipitation mechanism rather than to simple dissolution.

6. Dynamic fatigue susceptibility of sodium silicate glasses was found to increase with increasing water content in glass.

II. RESEARCH AND RESULTS

1. In the course of investigation of the effect of various coating materials on chemical durability of glasses, it was found that some chemicals in the solution can suppress the glass corrosion. In particular, calcium ions in alkali solution improved the chemical durability of silica glass by a factor of 3. This inhibitor effect of calcium was caused by deposition of calcium on glass surface and a film formation. A similar but less drastic effect was found for other alkaline earth elements in solution. In the chemical durability of glasses in static solution, this inhibitor effect is expected to play an important role.

When a heavy alkaline earth elements are included in the solution, severe surface flow was generated. This caused a precitous decrease in the mechanical strength of glass.

2. If fatigue is caused by stress corrosion, no fatigue should be observed when mechanical strength is tested in non-corrosive environment. Yet similar fatigue behavior was observed in water and in non-corrosive, water-free CCl_4, while the strength value was different in different liquids. To clarify the mechanism, strength was measured in a variety of liquids. The strength value was found to correlate with the surface energy of the glass estimated from the swelling of porous high silica glass immersed in the liquid. This observation appears to support the surface energy mechanism rather than the stress corrosion mechanism of fatigue.

3. Surface of high silica glass was treated with various chemicals to produce a hydrophobic surface and the dynamic fatigue tendency of the resulting glasses was investigated. Glasses treated with $(CH_3)_3SiCl$ or CH_3MgBr showed very little dynamic fatigue when measured in respective solutions.

4. The basic assumption of the popular stress-corrosion mechanism of fatigue is that the glass corrodes faster under tensile stress. According to the equation used in the stress-corrosion mechanism the corrosion rate should be slower under compression. To test this assumption, dissolution rate of silica glass under hydrostatic pressure was measured. To the contrary of the expectation, the dissolution rate increased with increasing hydrostatic pressure. This observation appears to contradict the stress-corrosion mechanism.

5. Strength of abraded glass usually increases when the specimens are held in water. This is explained by crack blunting due to the dissolution of glass in water. It was found that the strength increases faster when specimens are held in water containing silicic acid even though the dissolution rate is slower in such solution, indicating that the simple dissolution mechanism is inadequate. As an alternative, the dissolution and precipitation mechanism was suggested. In this mechanism, a portion of glass with large radius of curvature dissolves in water and the dissolved glass precipitates at a crack tip with small radius of curvature, reducing the stress concentration factor. This mechanism is possible since the solubility and dissolution rate are dependent upon the radius of curvature.

6. It is well known that water in atmosphere influences the fatigue characteristics greatly but it is not known what role the water in glass plays. Sodium silicate glasses with water content 16 ~35 wt% were prepared by drying soluble silicates and their dynamic fatigue characteristics were investigated in paraffin oil. It was found that the fatigue susceptibility increases with increasing water content. (cf. Appendix)

The most of the research results were reported in previous four annual reports of this project. Only the most recent result is attached as appendix.

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IV. PUBLICATIONS

1) "Relation of Surface Structure of Glass to HF Acid Attack and Stress State", M. Tomozawa and T. Takamori, J. Am. Ceram. Soc., 62 [7-8] 370 (1979).

2) "Calcium Deposition on Glass Surface as an Inhibitor to Alkaline Attack", Y. Oka, K.S. Ricker, and M. Tomozawa, J. Am. Ceram. Soc., 62 [11-12] 631 (1979).

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10) "Effects of Surface Conditions on Stress-Rate Dependence of Mechanical Strength of High Silica Glass", S. Ito and M. Tomozawa to appear in the Proceedings of the International Symposium on Fracture Mechanics of Ceramics (1982).

11) "Dynamic Fatigue of Sodium-Silicate Glasses with High Water Content", S. Ito and M. Tomozawa, to appear in J. de Phys. (1982)(Appendix).

V. ORAL PRESENTATION

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2) "Mechanism of Impurity Effect of Alkali Durability of Silicate Glasses", Y. Oka, K.S. Ricker and M. Tomozawa, The American Ceramic Society, Glass Division Fall Meeting, Bedford, PA, October, 1979.

3) "Swelling and Mechanical Strength of Glass", Y. Oka, Solid State Seminar, Rensselaer Polytechnic Institute, Troy, NY, February 1980.

4) "Swelling and Mechanical Strength of Glass", Y. Oka, J.M. Wahl and M. Tomozawa, XII International Congress on Glass", Alburquerque, NM, July 1980.

5) "Effect of Alkaline Earth Ion as a Inhibitor to Alkaline Earth on Silica Glass", Y. Oka and M. Tomozawa. Frontier of Glass Science, An International Conference, Los Angeles, CA, July 1980.

6) "Stress Corrosion of High Silica Glass", S. Ito and M. Tomozawa, 83rd Annual Meeting of the American Ceramic Society, Washington, D.C., May 1981.

7) "Surface Energy Effect on Strength of Glass", M. Tomozawa, NBS Symposium on Stress Corrosion, Washington, D.C., June 1982.

8) "Effect of Surface Conditions on Stress-Rate Dependence of Mechanical Strength of High Silica Glass", S. Ito and M. Tomozawa. International Symposium on Fracture Mechanics of Ceramics. State College, PA, June 1981.

9) "Surface Energy and Mechanical Strength of Glass", M. Tomozawa, Gordon Conference on Glass, Plymouth College, N.H., Aug. 1981.

10) "Microstructure of Glass Surface Reacted with Water", M. Tomozawa and S. Capella, The American Ceramic Society Glass Division Fall Meeting. Bedford, PA, October 1981.

11) "Crack Blunting of Silica Glass", S. Ito and M. Tomozawa, 84th Annual Meeting of the American Ceramic Society, Cincinnati, Ohio, May 1982.

12) "Dynamic Fatigue of Sodium-Silicate Glasses with High Water Content", S. Ito and M. Tomozawa, 5th International Conference: The Physics of Non-Crystalline Solids, Montpellier, France, July 1982.

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APPENDIX

DYNAMIC FATIGUE OF SODIUM-SILICATE GLASSES WITH HIGH WATER CONTENT

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Résumé - La résistance méchanique du verre depend de la vitesse d'application de la contrainte. Cette dépendence d'un verre du silicate de soude a été étudiée. On a préparé les verres en sechant la solution commerciale du silicate de soude dans un four ou dans un autoclave. La résistance méchanique des verres a été mesurée par une méthode de flexion en quatre pointes, a différentes vitesses d'application de la contrainte. Ces verres montrent alors une forte dépendance de la resistance sur la vitesse meme dans l'huile séchée. La dépendance augmente en augmentant l'eau. La valeur de n, measure de la dépendance, est à peu près cinq pour les verres avec $\sim$ 25% eau. En même temps, le module de Young a baissé en augmentant d'eau. Nous suggerons que le transport d'eau crée par la contrainte est responsable pour la dépendance accrue. De plus, la valeur apparente du module de Young a baissé en diminuant la vitesse d'application de la contrainte. On explique ce phenomèna a cause de la visco - élastcité des verres.

Abstract.- The stress-rate dependency of the mechanical strength of sodium silicate glass with high water content (up to $\sim$25% by weight) was investigated. The glasses were prepared by drying commercial sodium silicate solution in an oven or an autoclave. The mechanical strength of the glasses was measured by a four point bending method at various stress rates. These glasses showed a strong stress rate dependency even in dired paraffin oil and the dependency increased with increasing water content; the value of n, a measure of the stress rate dependency, was approximately 5 for glasses with $\sim$25 wt% water. At the same time Young's modulus decreased with increasing water content. It is suggested that stress-induced motion of water is responsible for the increased stress rate dependency. In addition, the apparent value of Young's modulus decreased with decreasing stress rate. This phenomenon was explained in terms of the visco-elastic property of the glasses.

1. Introduction.- Water in the environment is well known to affect the mechanical strength of glass [1,2]; the strength measured in water is about one half of that measured in vacuum [3], and the strength decreases with increasing loading time (static fatigue) and with decreasing stress rate (dynamic fatigue)[4]. On the other hand, very little is known about the effect of water in glass on its mechanical strength. Recently, Wu [5] reported some data showing that the elastic modulus and the strength of hydrated silicate glass decreased with increasing water content, while McMillan et al[6] reported that the bending strength of the soda-lime silica glass with a small amount of water (below 780 ppm) was not influenced by the water content. So far, no research has been reported on details of the effect of the water in glass on the strength, especially on fatigue phenomenon.

In this study, the stress rate dependency of the mechanical strength and the elastic modulus of the sodium silicate glass with high water content were investigated.

2. Experiment.- The glasses with high water content were prepared by drying commercial sodium silicate solution (Na_2O $\sim$8.9 wt%, SiO_2 $\sim$28.7 wt%, H_2O $\sim$62.4 wt%; $Na_2O \cdot 3.3SiO_2 \cdot 24H_2O$ by mole ratio) in an oven at 50$\sim$80°C for 5$\sim$7 days in air (for

specimens with H_2O greater than 20 wt%) and then in an autoclave at $80^o \sim 150^oC$ for $3 \sim 5$ days in ~ 30 bar N_2 (for specimens with H_2O less than 20 wt%). The water contents of these glasses were determined from weight loss by drying the glass at 400^oC for 2h. The dry glass ($Na_2O \cdot 3.3SiO_2$, by mole ratio) was prepared by heating the glass with high water content at 400°C for 2h and subsequently melting the dried powder at 1450^oC for 5h. The glass was annealed at 530^oC for 2h. The water content of the dry glass was determined approximately from the peak intensity of IR spectra [7]. The glasses were cut into samples ~ 1.7 mm thick, ~ 3.5 mm wide, ~ 25 mm long with a diamond saw. The surface of the specimen was polished with SiC paper (600 grit). Prior to the mechanical strength measurement, the center region of one surface was abraded by a rougher SiC paper (240 grit), in a direction perpendicular to the long axis of the specimen. This surface was placed on the tension side during the mechanical testing. All the polishing and abrading were performed in paraffin oil.

The mechanical strength was measured by a four point bending method at five different crosshead speeds ($1.27 \sim 0.00254$ cm/min.) at room temperature. The testing was done in paraffin oil which had been dried using P_2O_5 for one week, to eliminate the effect of environmental water. At least 7 specimens were used to obtain one data point.

The Knoop hardness number was measured with a Kentron microhardness tester at room temperature. The glass surface was polished, using diamond paste. Within 15 min. after polishing, the indenter was brought into contact with the glass surface for 30 s. with a 200 g load. The length of the long diagonal of the indentation was measured immediately after removing the load.

3. Result and Discussion.- Fracture strength vs. stress rate as a function of water content in the glass is shown in Fig. 1. The glasses with high water content showed a strong stress rate dependency of the fracture strength, even though the strength was measured in paraffin oil. The dependency increased with increasing water content; the value of n [8], which was calculated from the slope of the lines in Fig. 1, decreased with increasing water content. On the other hand, the dry glass showed little stress rate dependency.

In Figure 1, the strength of the abraded dry glass was seen to be lower than that of the glass with 15.9 wt% H_2O, while the general trend appears to be lower strength for higher water containing glasses. This apparent discrepancy is probably due to the difference in the surface microcrack geometry caused by the different hardness. Figure 2 shows the Knoop hardness vs. water content. The hardness decreases with increasing water content of the glass. Thus it is

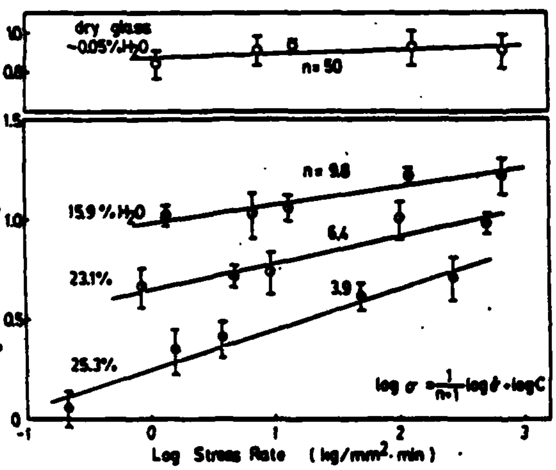

FIG. 1. Fracture strength vs. stress rate for glasses with various water contents. (Measured in paraffin oil at room temperature; ± standard deviation)

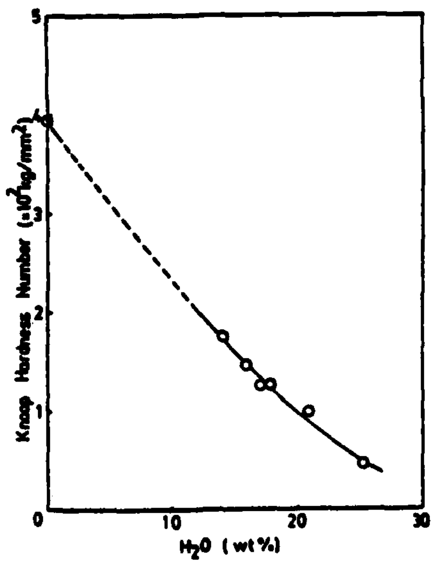

FIG. 2. Knoop hardness number vs. water content in glass.

expected that a glass with high water content would deform easily and a microcrack on its surface would have a more rounded tip than that of a dry glass. In fact it was observed that the abraded surface of the specimens with high water content became smooth indicating the healing effect. If the crack geometry is the same, the strength of the dry glass would probably be higher than that of the glass with 15.9 wt% H_2O.

Some glasses used in this study showed an apparent Young's modulus which varies with crosshead speed as shown in Fig. 3. For the highest water content (~25 wt% H_2O), and the low crosshead speed, in addition, apparently non-brittle fracture was observed as shown in the lower curves in Fig. 3.

The apparent Young's modulus value was calculated from the load and the deflection of the specimen [9] and is shown in Fig. 4 as a function of stress rate. From the figure, it is seen that the modulus decreases with increasing water content and the moduli of the glasses containing 23.1% and 25.3% water were markedly dependent on the stress rate, while the moduli of the dry glass and the glass containing 15.9 wt% water were independent of the stress rate. These results suggest that the glass with high water content shows visco-elastic behavior. Using two parallel Maxwell models [10], the viscoelastic behavior was analyzed and the elastic modulus at infinite stress rate was calculated and is shown in Fig. 5. The modulus decreased gradually up to ~20 wt%, and then rapidly with increasing water content. This can be attributed to the gradual loosening of the glass structure due to the increasing number of broken ≡Si-O- bonds by water. Beyond 20 wt% H_2O, structural loosening becomes accelerated since the glass transition temperature approaches room temperature [11] where all the measurements were made.

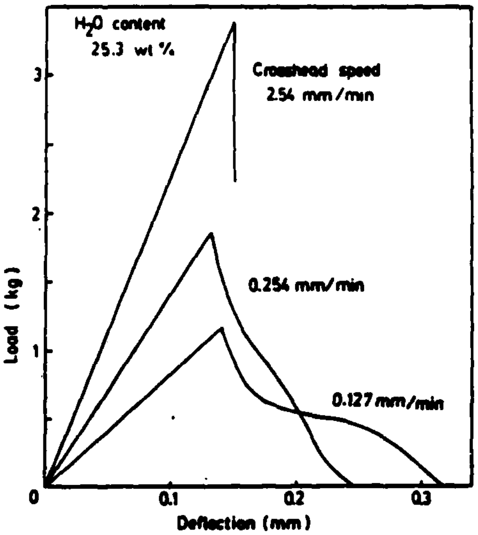

FIG. 3. Load vs. deflection at various crosshead speeds for glass with 25.3 wt% water.

The stress rate dependency of the strength, namely, dynamic fatigue, has been usually explained by a corrosion reaction [1] of the glass with atmospheric water or a surface energy reduction [12,13] due to water adsorption. However, in this study, the effect of the water in the environment is considered negligible, since the strength was measured in dried paraffin oil and in fact, the n value of the dry glass, 50, was much higher than the usual n value [4] measured in the presence of water. This observation suggests that the dynamic fatigue of the glass containing water is induced by the water in the glass.

It is not clear whether or not the observed viscoelastic behavior has an influence on the stress-rate dependency of the strength. However, as shown in Fig. 1, the glass containing 15.9 wt% water shows dynamic fatigue, even though it shows elastic behavior (in Fig. 4), indicating that the fatigue tendency is accelerated by water in glass even when viscoelastic behavior is absent.

Generally, stress is known to cause diffusion [14], and alter the local concentration [15,16] of the solute in the solid. Therefore, when a load is applied to the glass with high

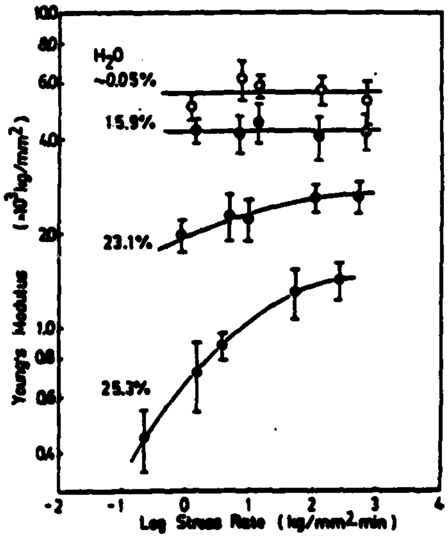

FIG. 4. Apparent Young's Modulus vs. stress rate for glasses with various water contents.
(± standard deviation)

water content, the water in the glass is expected to diffuse to a crack tip, where a large tensile stress exists because of the stress concentration. It is possible that the water diffused to the crack tip reduces the strength of the glass causing the dynamic fatigue phenomenon. For example, there are indications [17,18] that the fracture toughness decreases with decreasing Young's modulus, at least for homogeneous glasses. Since Young's modulus was found to decrease with increasing water content, the strength of the glass would decrease with increasing amount of diffused water. The diffusion coefficient of water is expected to increase with water content. This would make the strength of the glasses with higher water content more stress rate susceptible, as was observed here.

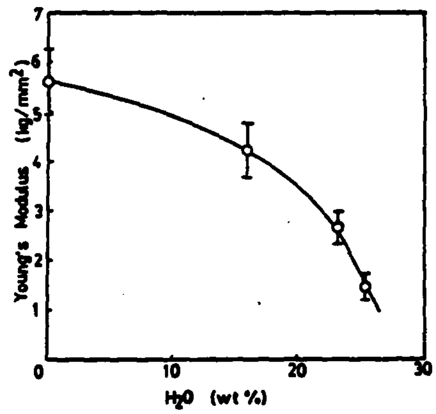

FIG. 5. Young's modulus at infinite stress rate vs. water content in glass (± standard deviation).

4. Conclusion.- The water in the glass promotes the stress rate dependency (dynamic fatigue) of the mechanical strength and the visco-elastic phenomena, which makes the apparent Young's modulus value stress rate dependent.

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